Thick Low-Cost, High-Power Lithium-Ion Electrodes via Advanced Processing

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National Transportation Research Center

2020 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 1-4, 2020 **Project ID: BAT164**

Overview

Timeline

- Task Start: 10/1/14
- Task End: 9/30/22
- Percent Complete: 75%

Barriers

- Barriers Addressed
  - **By 2022, further reduce EV battery-pack cost to $80/kWh.**
  - **Advanced Li-ion xEV battery systems with low-cost electrode architectures.**
  - **Achieve deep discharge cycling target of 1000 cycles for EVs by 2022.**

Budget

- $400k in FY19
- $350k in FY20

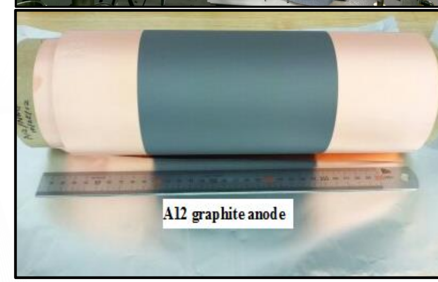
Partners

- Interactions/Collaborations
  - National Laboratories: ANL, SNL, INL
  - Universities: KIT, SUNY-Binghamton, University of Picardy Jules Verne
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Material Suppliers: PPG Industries, TODA America, Superior Graphite, IMERYS, JSR Micro, Solvay Specialty Polymers, Ashland, Forge Nano
  - Equipment Manufacturer: Frontier Industrial Technology, B&W MEGTEC
- Project Lead: ORNL

Relevance & Objectives

- Main Objective: To improve cell energy and power density and reduce battery pack cost by manufacturing thick electrodes with tailored electrode architecture via advanced processing and high-energy, high-voltage cathode materials.

- Objectives in this period
  - Apply aqueous processing to Ni-rich layer oxides (NMC811 and NCA)
  - Fabricate thick (6-8 mAh/cm^2), crack-free composite NMC811 cathode via aqueous processing
  - Create laser structured electrodes
  - Characterize electrolyte imbibition rate and understand the electrolyte imbibition-processing relationship
  - Assemble pouch cells with NMC811 and thick, tailored electrode architecture
  - Demonstrate energy density ≥225 Wh/kg (BMF pouch cell level)



Project Milestones

Status	SMART Milestones	Description
9/30/19 ✓	Go/No-Go Decision	Complete 1.5-Ah pouch cell rate performance for cells with combined Gen 3 graphite anode and NMC811 cathode structured designs. Improved gravimetric energy density of baseline cell design to >250 Wh/kg (cell level) and demonstrate no more than 40% capacity fade through 500 USABC 0.33C/-0.33C cycles. Demonstrate 40% of rated capacity at 2C discharge rate verifying high power density.
3/31/20 Delayed by 3 months due to facilities upgrade and COVID-19 stand-down.	Annual Milestone (stretch)	Quantify impedance (via AC impedance technique) of Gen 3 structured, multilayer anode and cathode coatings (multi-pass, dual slot-die coated, etc. at 8 mAh/cm^2) with different individual layer thicknesses and different total thicknesses to achieve >250 Wh/kg improvement in cell energy density; verify long-term performance by achieving no more than 40% capacity fade through at least 500 USABC 0.33C/-0/33C cycles. Demonstrate 40% of rated capacity at 2C discharge rate to show preservation of power density.
9/30/20 On track	Annual Milestone (regular)	Freeze cast both a 250-micron solid-state LLZO electrolyte (with 10-micron dense layer and 240-micron porous layer) and conventional thick LIB NMC 811 cathode (200 microns) with vertically aligned pore structure and successfully complete sublimation and infiltration steps.

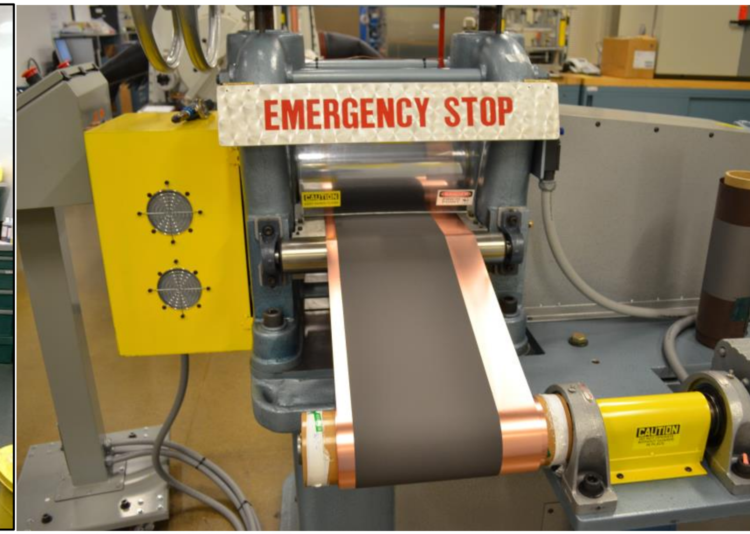
Project Approach

- Problems:
  - Cost effective methods of producing thick electrode architectures
  - Cracking of thick coatings with water as solvent
  - Lithium-ion mass-transport limitations thick electrodes

- Technical approach and strategy:
  - Evaluate stability of high-energy and high-voltage cathodes (NMC811, LMO, NCA) during aqueous processing
  - Incorporate aqueous processing to fabricate NMC811 and NCA cathodes
  - Fabricate crack-free NMC811 cathodes with high areal loading (6-8 mAh/cm^2) via aqueous processing
  - Create laser structured electrodes to overcome Li^+ mass transport limitations
  - Simulate energy and power density improvements of laser structured electrodes
  - Characterize surface energy of composite electrodes and electrolyte imbibition into porous electrodes
  - Characterize advanced electrode microstructures
  - Evaluate rate performance and long term cyclability at room temperature and high temperature in BMF pouch cells

Project Approach – Pilot-Scale Electrode Processing and Pouch Cell Evaluation: DOE Battery Manufacturing R&D Facility (BMF) at ORNL

Planetary Mixer (≤2 L)



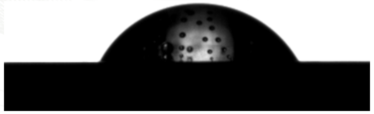
<u>Dry room for pouch cell assembly</u>

- Largest open-access battery R&D facility in US.
- All assembly steps from pouch forming to electrolyte filling and wetting.
- 1400 ft^2 (two 700 ft^2 compartments).
- Humidity <0.5% (-53°C dew point maintained).
- Pouch cell capacity: 50 mAh – 7 Ah.
- Single- and double-sided coating capability.
- Current weekly production rate from powder to pouch cells is 50-100 cells.

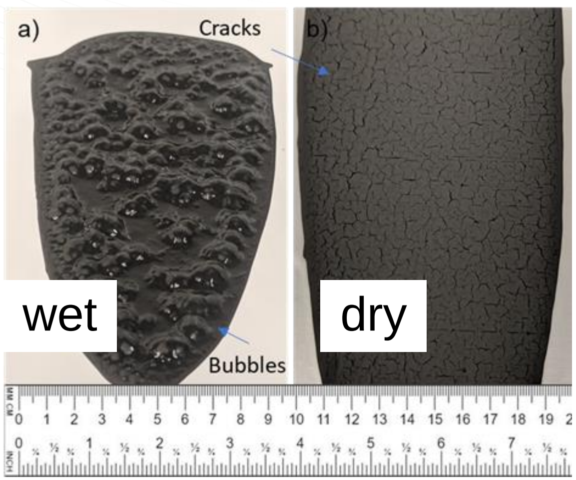
Technical Accomplishments – Executive Summary

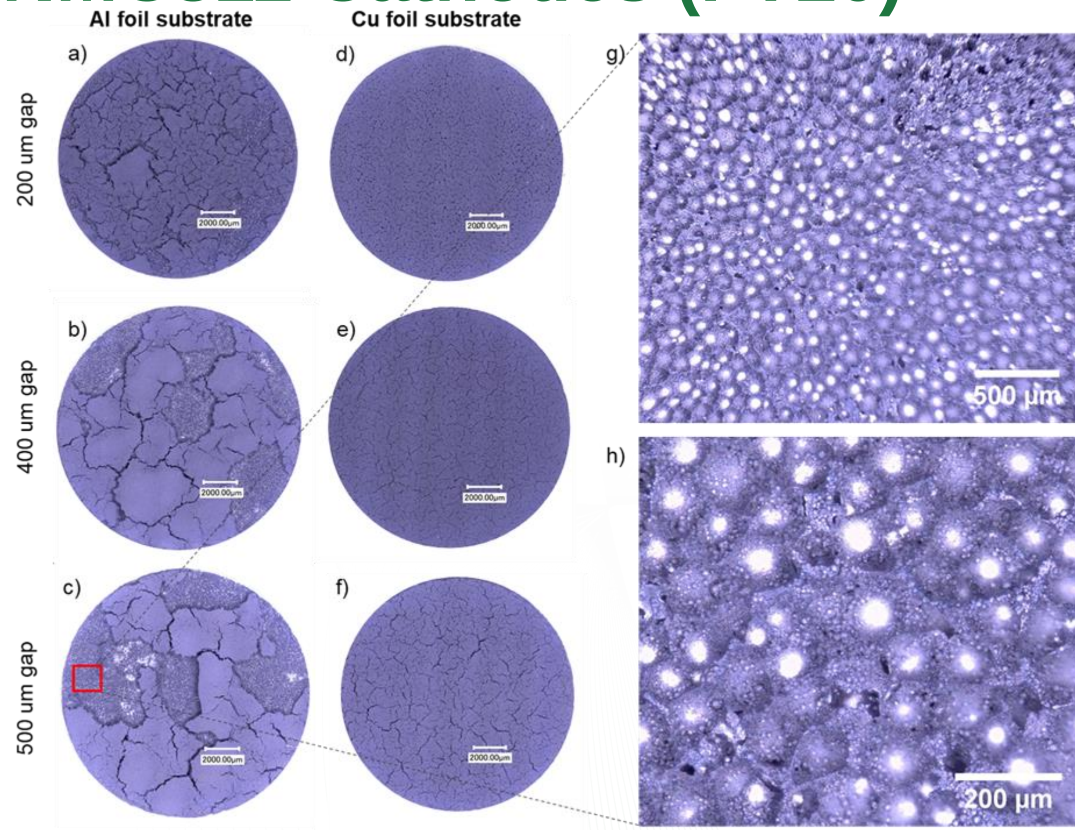
- Applied aqueous processing to fabricate NCA and thick NMC811 cathodes.
- Characterized compatibility of LFP, LCO, LMO, NMC532, and NCA with water.
- Elucidated the cracking formation mechanism in aqueous processed NMC811 cathodes; identified H_2 gas evolution due to Al corrosion as the main reason for electrode cracking.
- Eliminated cracks in aqueous processed NMC811 utilizing carbon fiber, smaller NMC811 and co-solvent approach.
- Optimized H_3PO_4 (PA) content in fabricating thick NMC811 cathode via aqueous processing for reducing active material Li leaching and Al foil corrosion.
- Created 2-layer, structured (6 mAh/cm^2 and 8 mAh/cm^2) NMC811 cathodes to improve rate capability in collaboration with ANL project BAT167.
- Demonstrated improved rate capability of laser structured NMC811 cathodes (6 mAh/cm^2) in collaboration with KIT, Germany.
- Fabricated crack-free NCA cathode via aqueous processing and achieved comparable performance to NMP/PVDF baseline.
- Correlated electrolyte imbibition relationship with processing and electrolyte formulation.

Technical Accomplishments— Identified Gas Evolution as the Main Reason for Electrode Cracking in Aqueous Processed NMC811 Cathodes (FY20)



Bubble formation

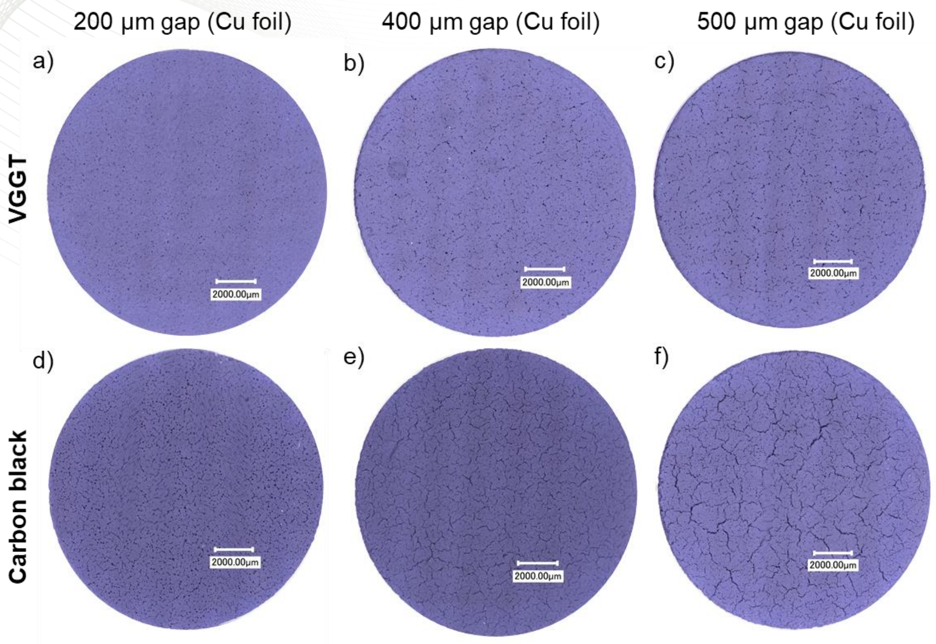


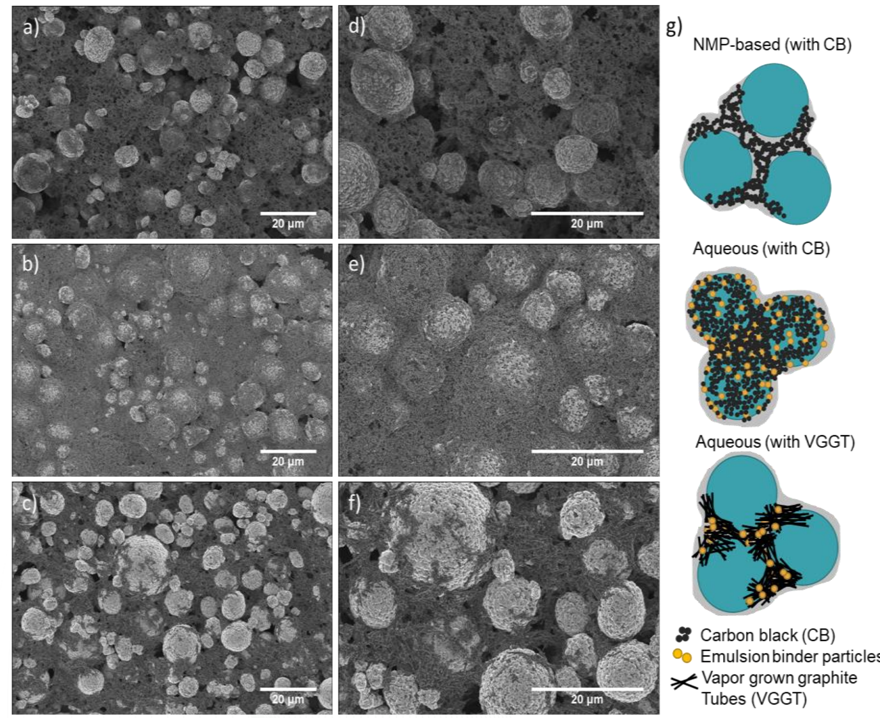


- NMC811 slurry is basic (pH>12) and significant H_2 bubbles are generated when coating on Al foil.
- Bubble generation and electrode cracking are dramatically suppressed when switching from Al foil to Cu foil:
  - H_2 gas evolution due to Al foil corrosion is the main reason for electrode cracking
  - Eliminating gas formation can prevent cracking

Sahore et al., ACS Sustainable Chemistry & Engineering 8 (8) (2020), 3162

Technical Accomplishments—Further Reduced Microcracks in Thick Aqueous Processed NMC811 Cathodes Utilizing VGGTs (FY20)

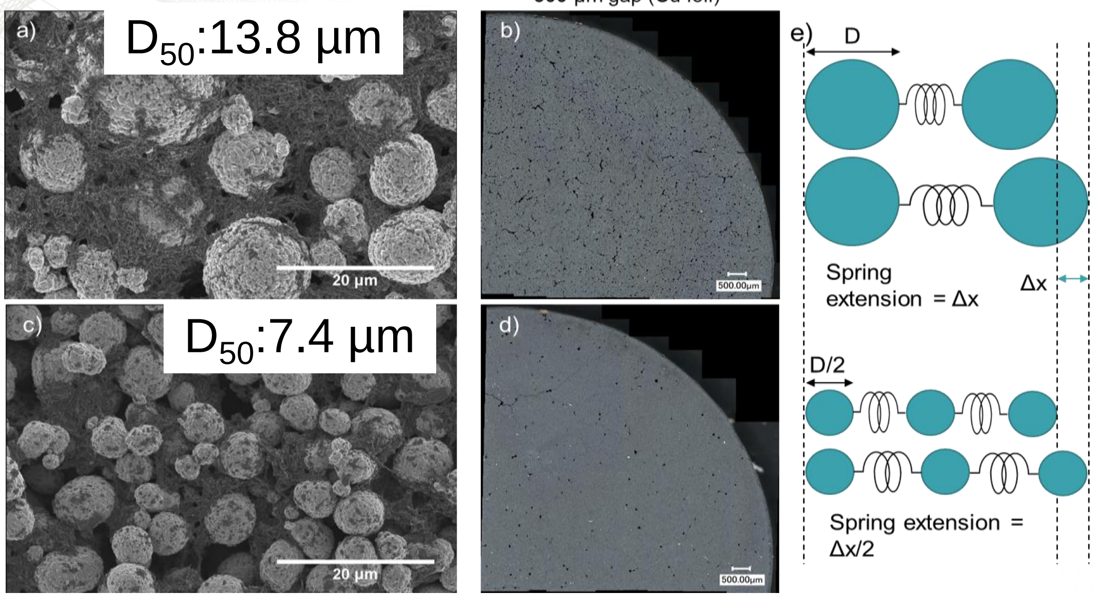




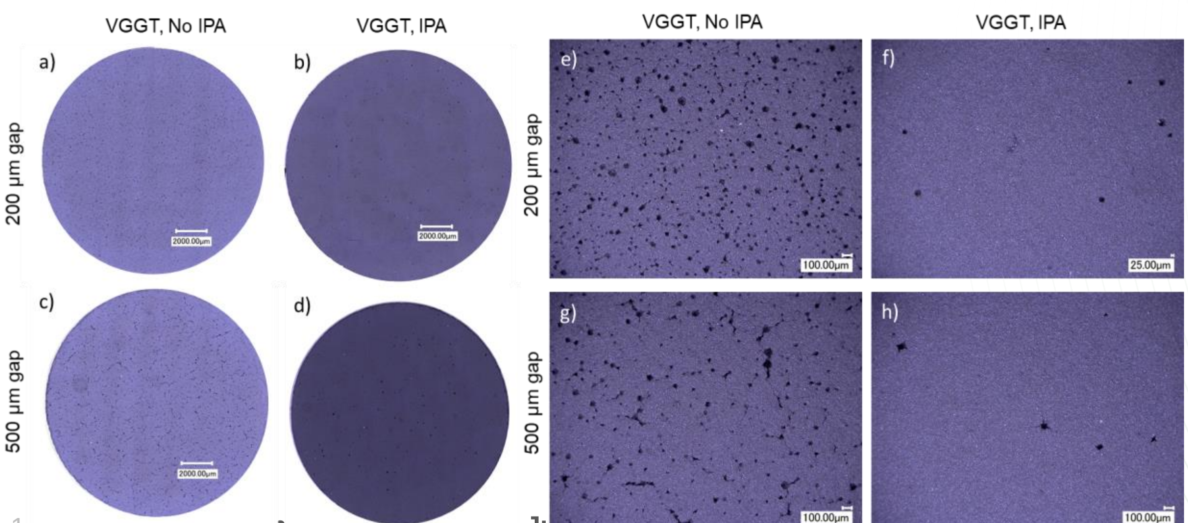
- Defects, i.e. tiny cracks, form within thick aqueous processed NMC811 cathode even coated on Cu foil:
  - Replacing carbon black with vapor-grown graphite tubes (VGGTs) dramatically reduces microcracks
  - NMC811 particles are covered thoroughly with the carbon black and binder network
  - The binder and VGGT network is located between NMC811 particles like the NMP processed cathode → higher cohesion

Sahore et al., ACS Sustainable Chemistry & Engineering 8 (8) (2020), 3162

Technical Accomplishments— Further Reduced Microcracks in Thick Aqueous Processed NMC811 Cathodes Utilizing Co-Solvent (FY20)



Reducing NMC811 particle size reduces the strain on the network as the NMC particles themselves are not stretchable.



Adding 12 wt% isopropyl alcohol (IPA) reduces surface tension and stress in dried NMC811 cathode further eliminating microcracks.

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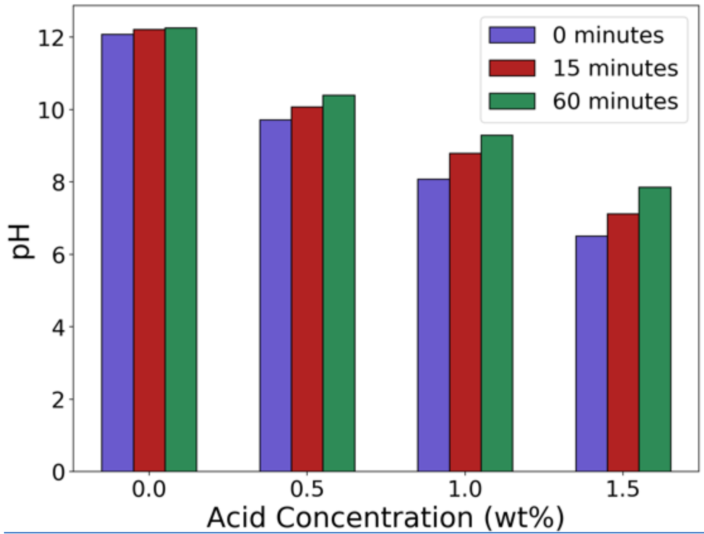
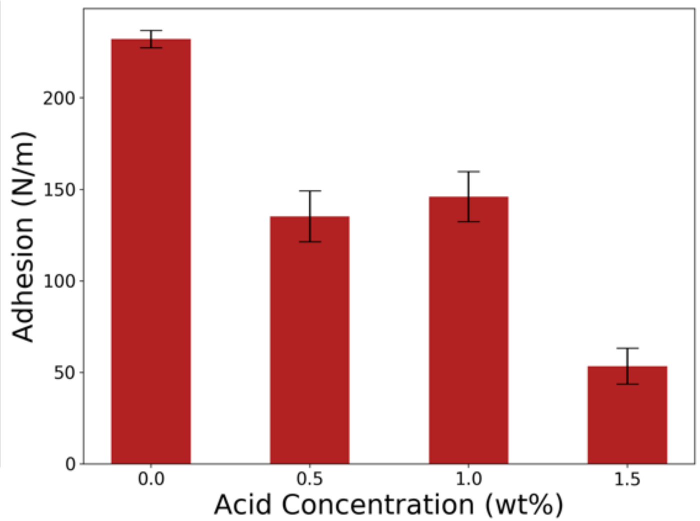
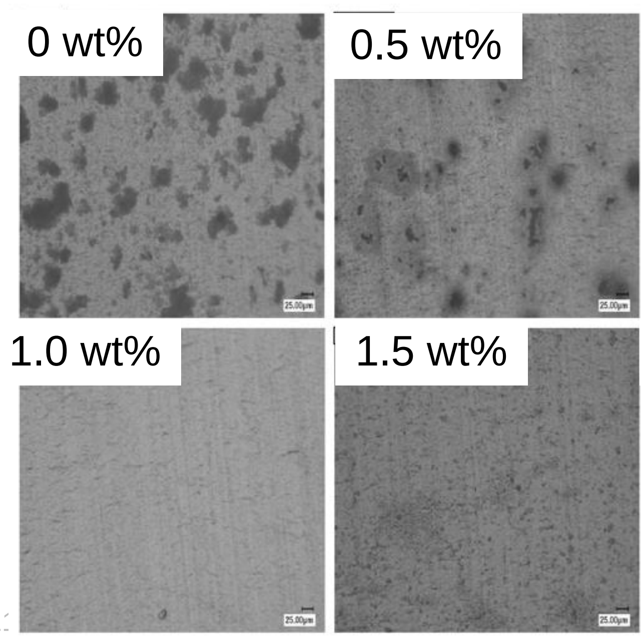
Sahore et al., ACS Sustainable Chemistry & Engineering 8 (8) (2020), 3162

Technical Accomplishments—Optimized H_3PO_4 (PA) Content in Fabricating NMC811 Cathode (FY20)

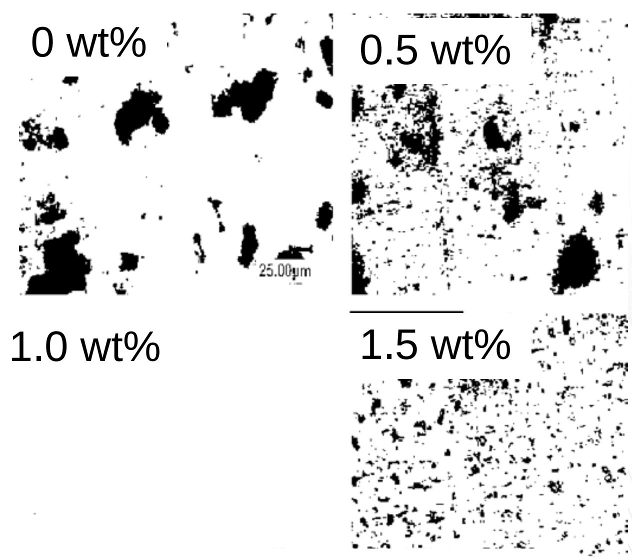




- Phosphoric acid (PA) was used to control slurry pH and avoid corrosion on Al foil.
- PA content up to 1.5 wt% in cathode formulation was investigated.
- PA content needs to be >1 wt% to avoid Al corrosion.
- Adhesion strength decreases with increasing PA content.



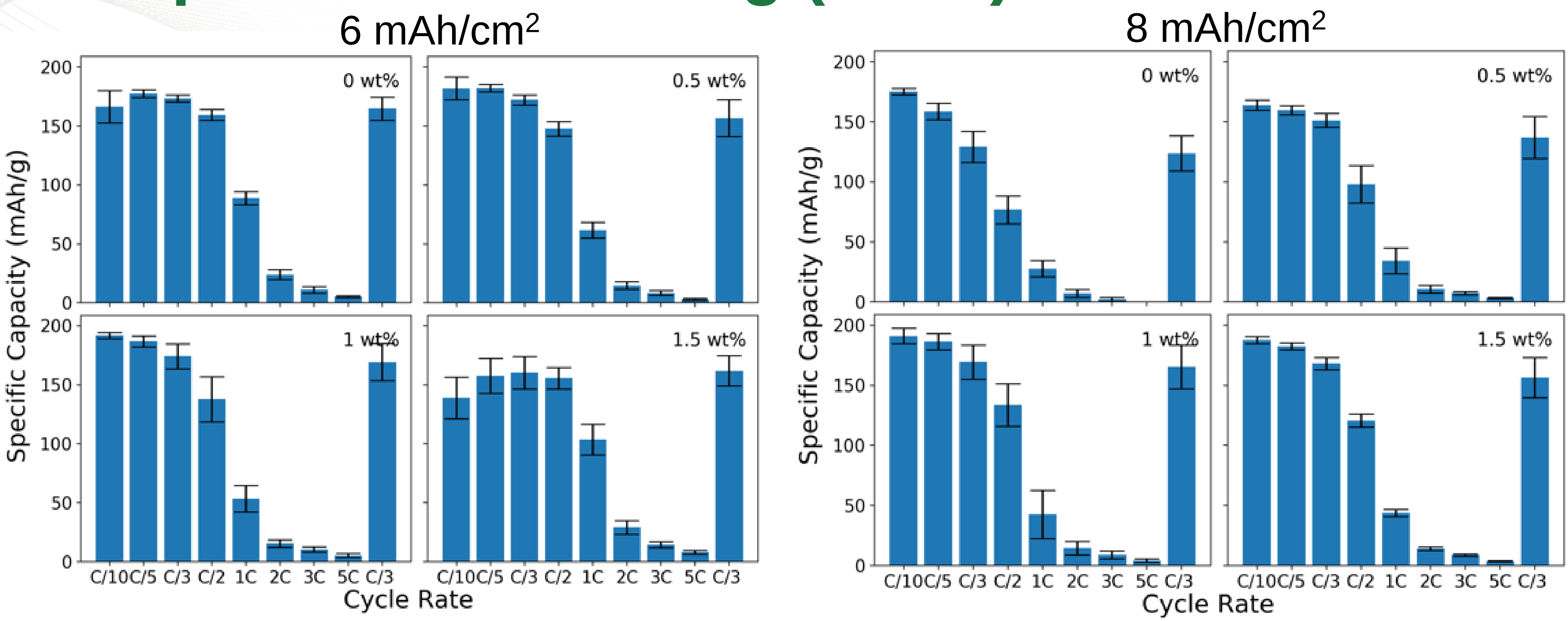
Al substrate from peeled off NMC811 with various PAA%



Binary threshold (42%)

- Corrosion area on Al foil was characterized after peeling off cathode.
- Minimal corrosion was observed with 1.0 wt% PA.

Technical Accomplishments—Successfully Fabricated NMC811 Cathodes with 6-8 mAh/cm^2 via Aqueous Processing (FY20)



- NMC811 cathodes with 6-8 mAh/cm^2 areal loading were fabricated with H_3PO_4 (PA) (at 0, 0.5, 1.0, or 1.5 wt% levels) via aqueous processing:
  - 90 wt% NMC 811 (Targray) 5 wt% carbon black (Denka Li-100) and 5 wt% binder mixture
  - Binder was 1:4 wt ratio of carboxymethylcellulose (CMC) and acrylic emulsion binder (JSR TRD202A)
- Excellent electrochemical performance was observed albeit with high liquid-phase Li^+ mass-transport limitations at high rates.

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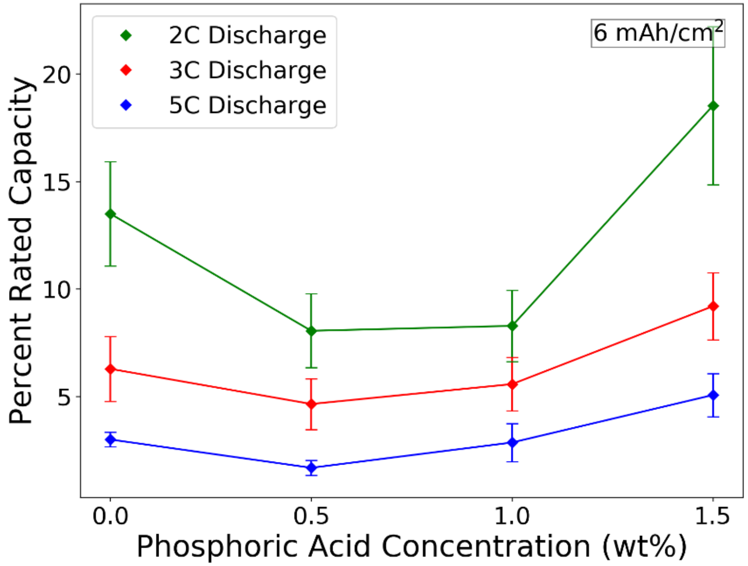
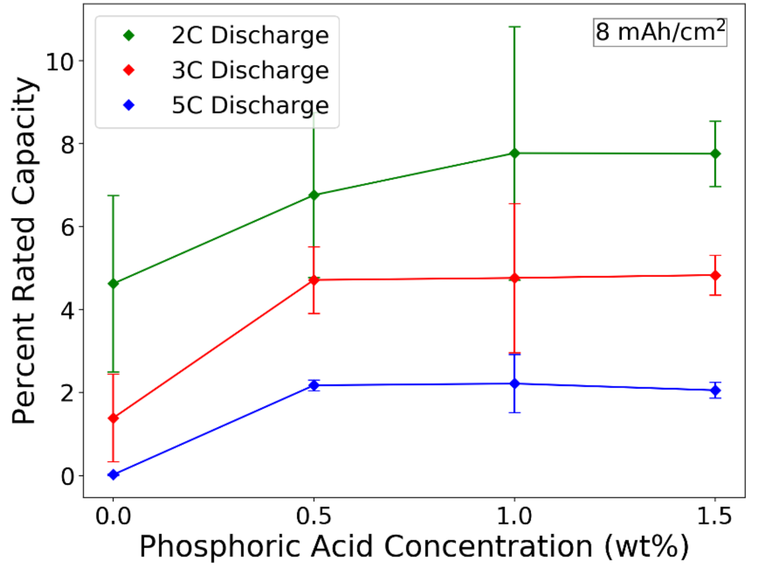
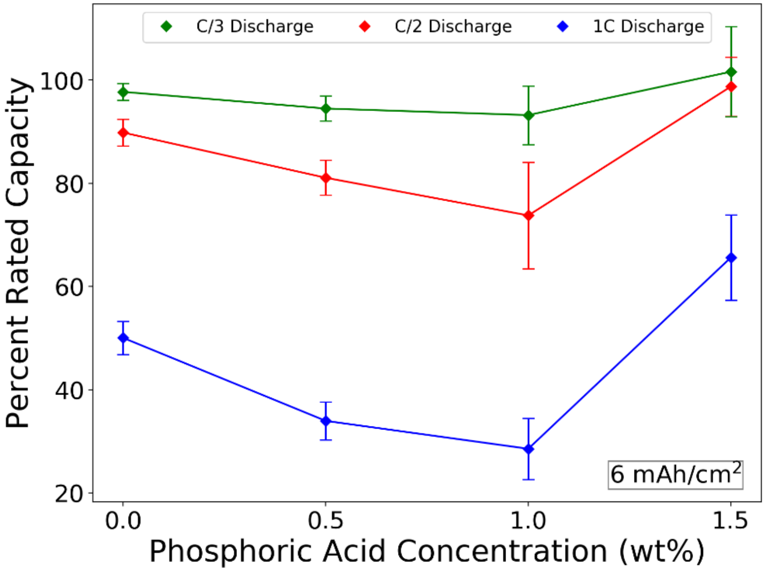
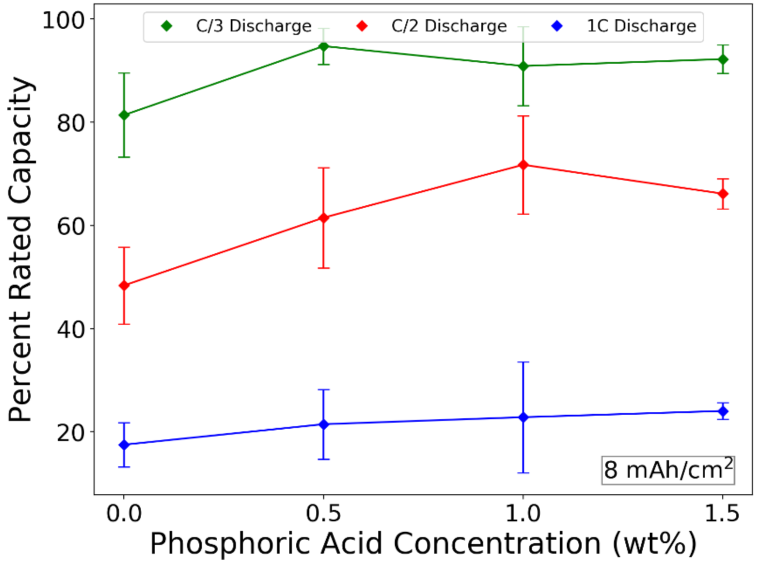
Technical Accomplishments—NMC811 with 1.5 wt% PA Demonstrated the Best Performance for 6-8 mAh/cm² (FY20)





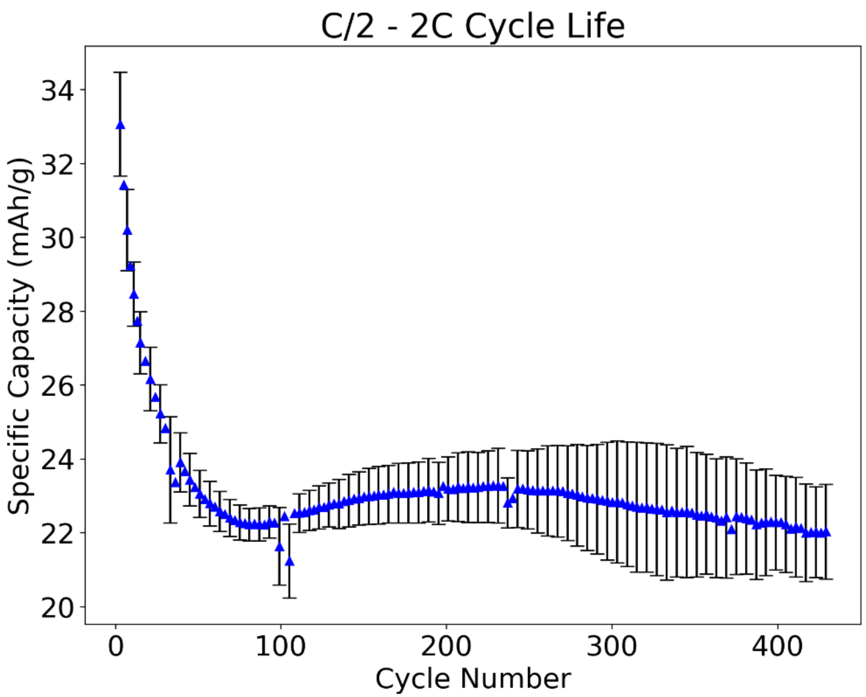
High Rate

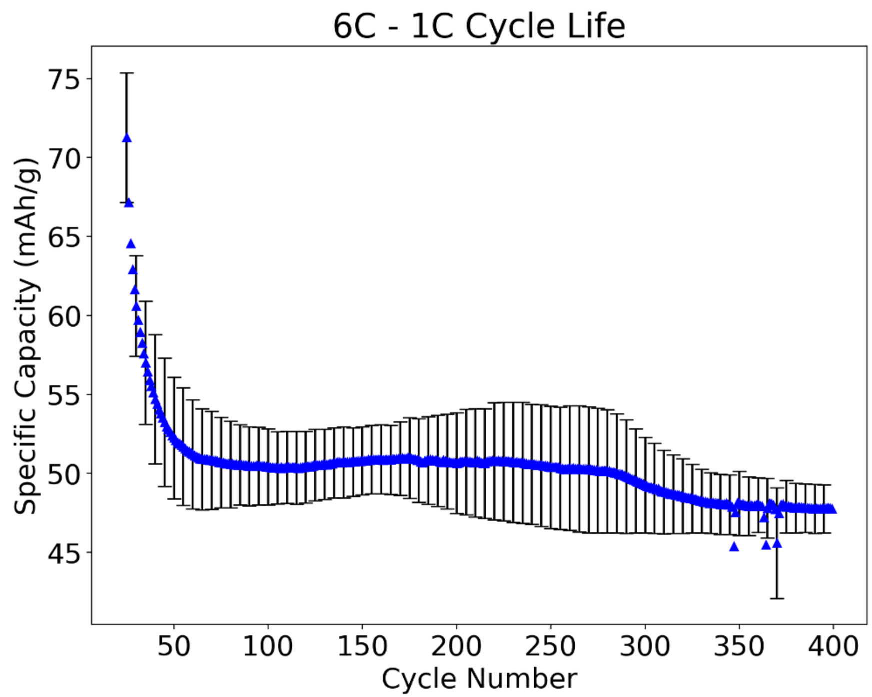




Low Rate

FY19 Q4 Go Decision Met – High-Rate Long-Term Cycling of 6-mAh/cm² Bilayer Cathodes



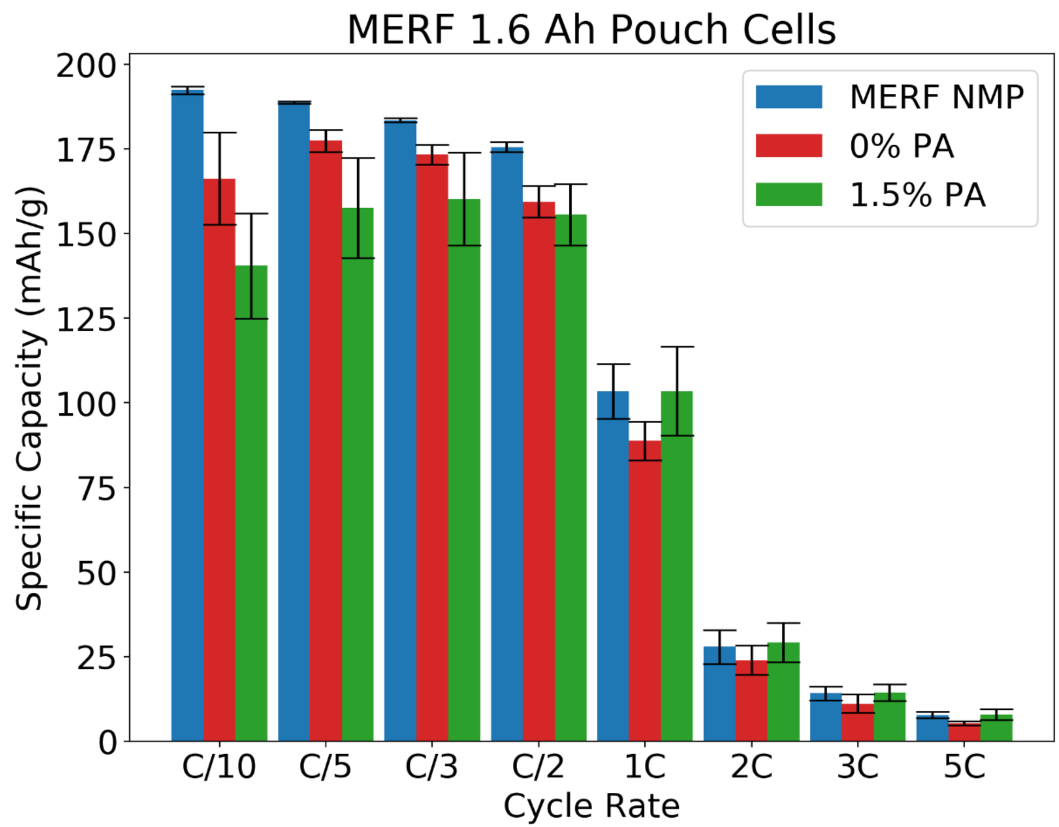


- **Achieved 66.6% capacity retention after 450 0.5C/-2C cycles (target was ≥60% retention at 0.33C/-0.33C).**
- **Achieved 67.0% capacity retention after 400 6C/-1C XFC cycles (no target was specified in FY19 as this was additional work).**
- **Met 1C discharge target of ~55% of rated capacity.**
- **Did not yet meet capacity target of 40% rated capacity at 2C → *only 15-16% achieved because a structured anode is required.***

Technical Accomplishments—Created 2-Layer Structured 6 mAh/cm^2 NMC 811 Cathodes for Improved Rate Performance (FY20)

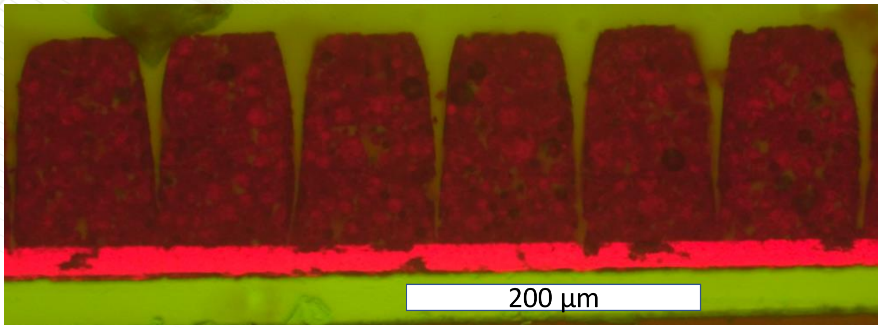
- **Blue:** 1.6 Ah cells with MERF cathode particles
  - NMP processed (double-pass coating)
  - Structured Cathodes
    - Large (Targray) 12-µm particles against Al foil
    - Small (MERF) 7.4-µm particles against separator
- **Red:** 0 wt% Phosphoric Acid (PA)
  - Aqueous Processed
  - All Targray 12-µm particles
  - Single-pass coating
- **Green:** 1.5 wt% PA
  - Aqueous Processed
  - All Targray 12-µm particles
  - Single-pass coating

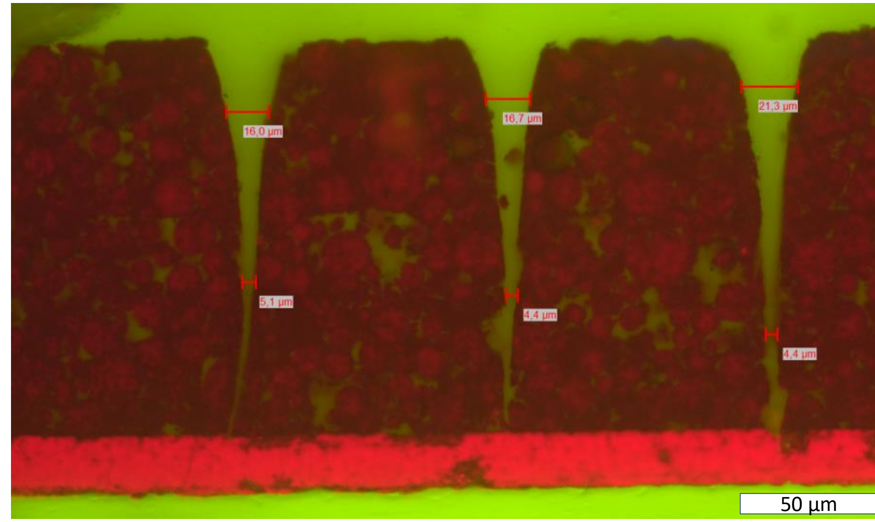
No Structured Anodes Used

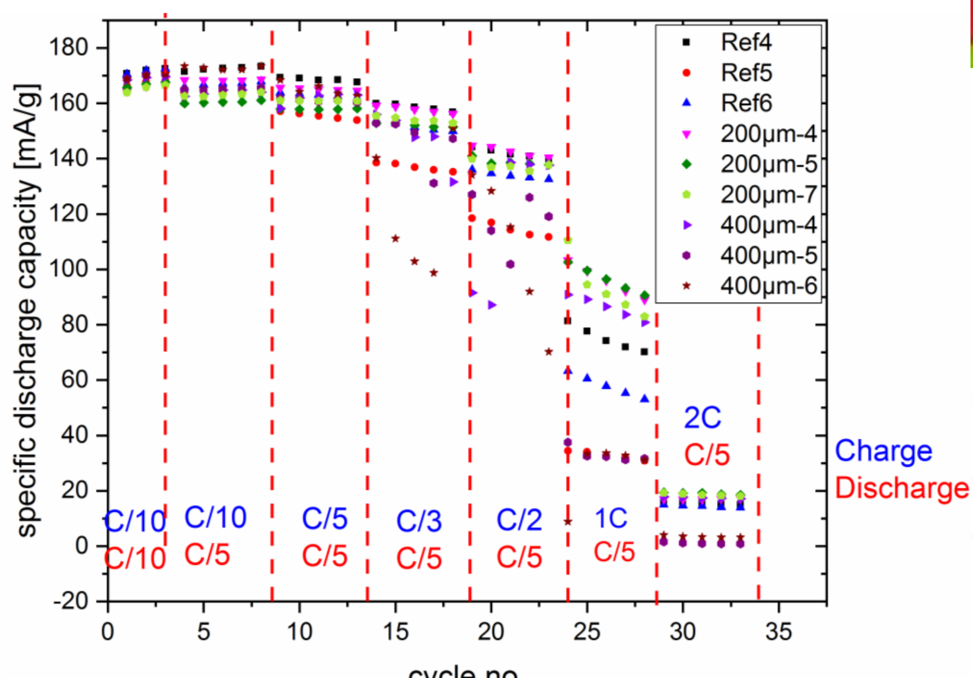


In collaboration with BAT167: Process Development and Scale-Up of Advanced Active Battery Materials

Technical Accomplishments—Demonstrated Improved Rate Performance in Thick NMC811 Cathode via Laser Structuring (FY20)

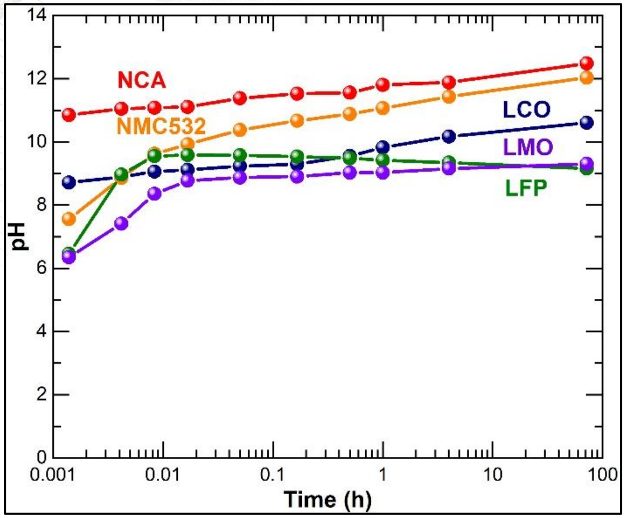


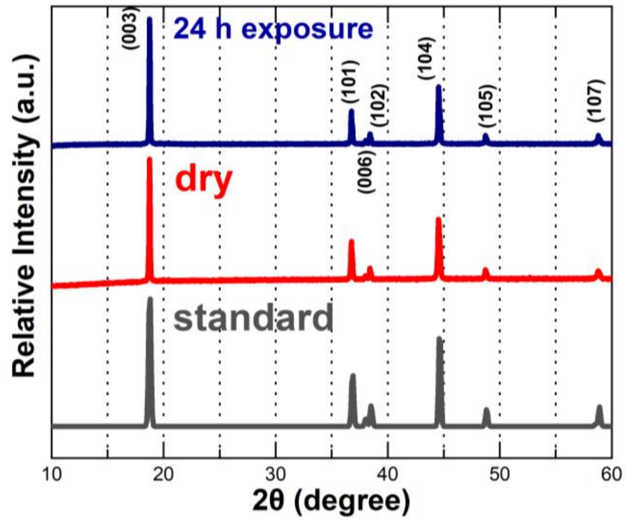


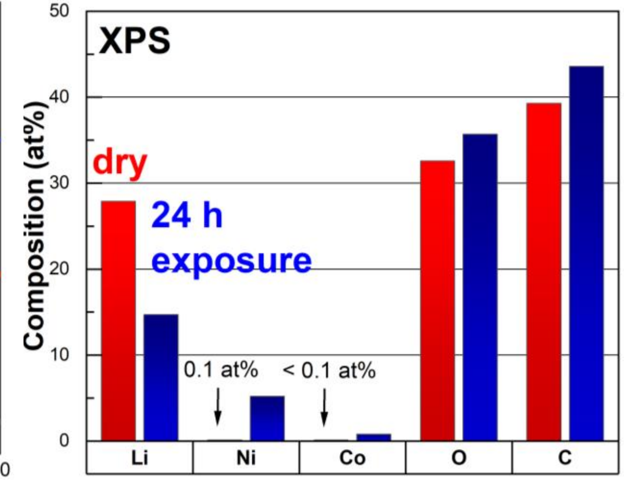


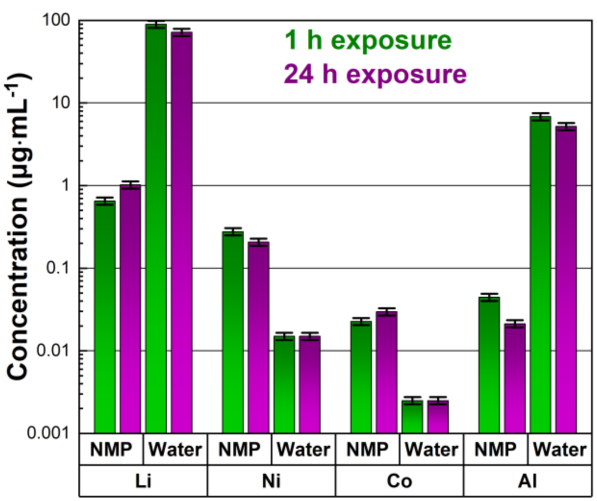
- Laster structured thick NMC811 (6 mAh/cm^2) with pitch size of 200 µm and 400 µm and channel width of 5-20 µm.
- The structured cathode showed improved rate performance when charged at C/2 and higher.

Technical Accomplishments—Demonstrated Comparable Performance from Aqueous Processed NCA Cathode(FY20)

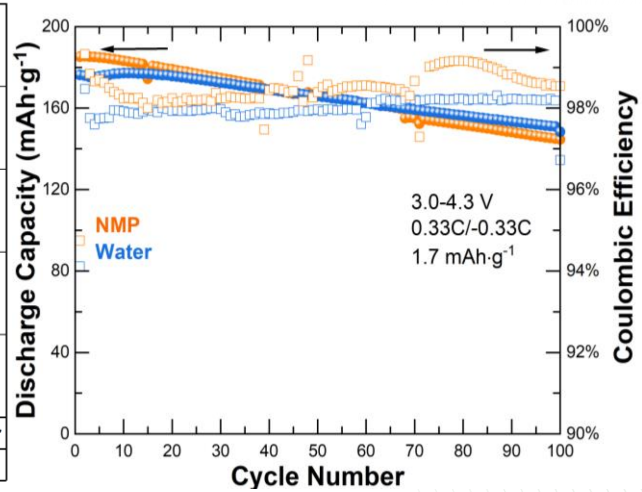








ICP-MS

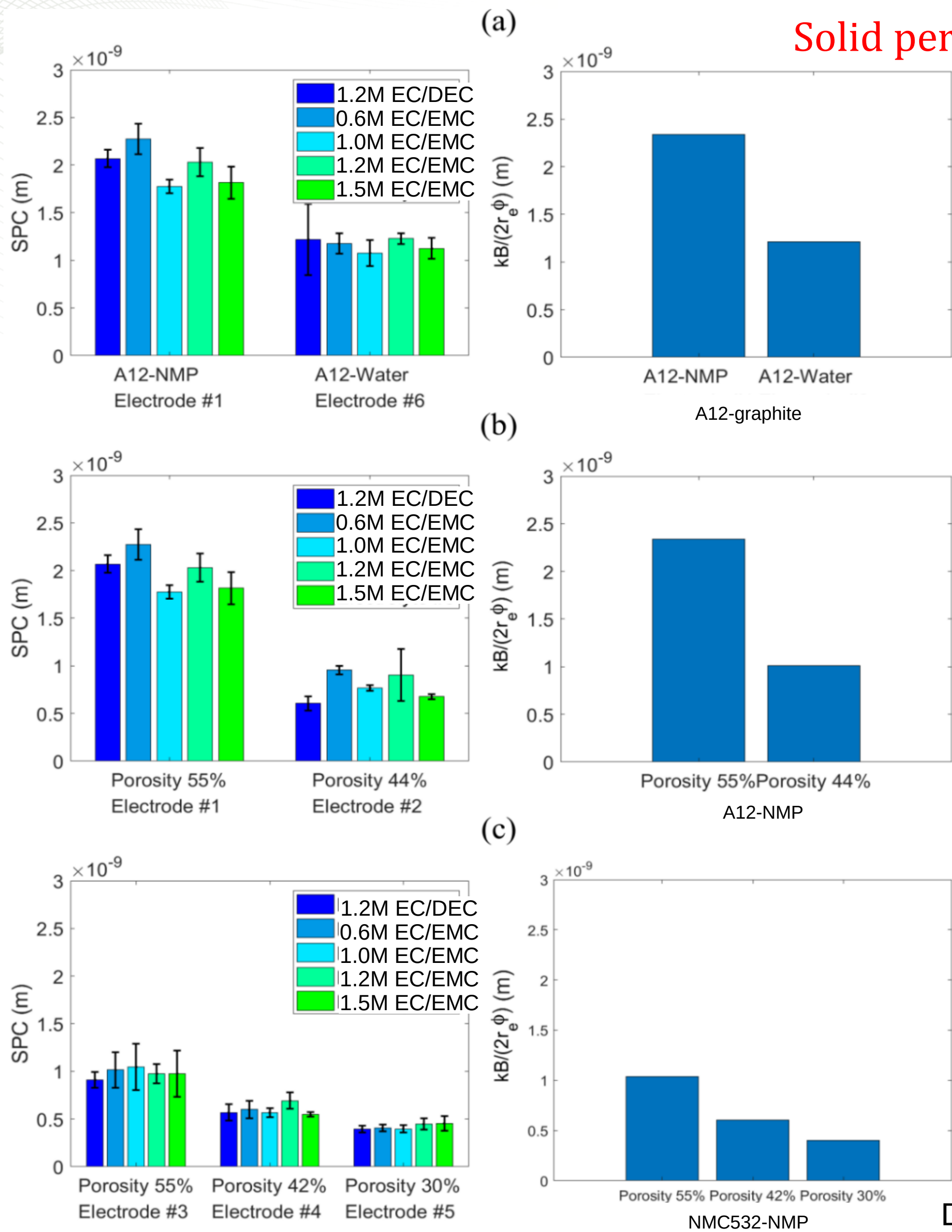


- 5 cathodes were investigated and all slurries were basic.
- No significant change to bulk structure.
- Surface Li content reduced after exposing active material to water.
- Li dissolution is 100× in water.
- Crack-free NCA cathode was fabricated with PAA as pH modifier.
- Comparable performance to NMP/PVDF was observed.

Hawley et al., *Journal of Power Sources*, Under review

Technical Accomplishments—Understanding of Electrolyte Imbibition-Processing Relation (FY20)

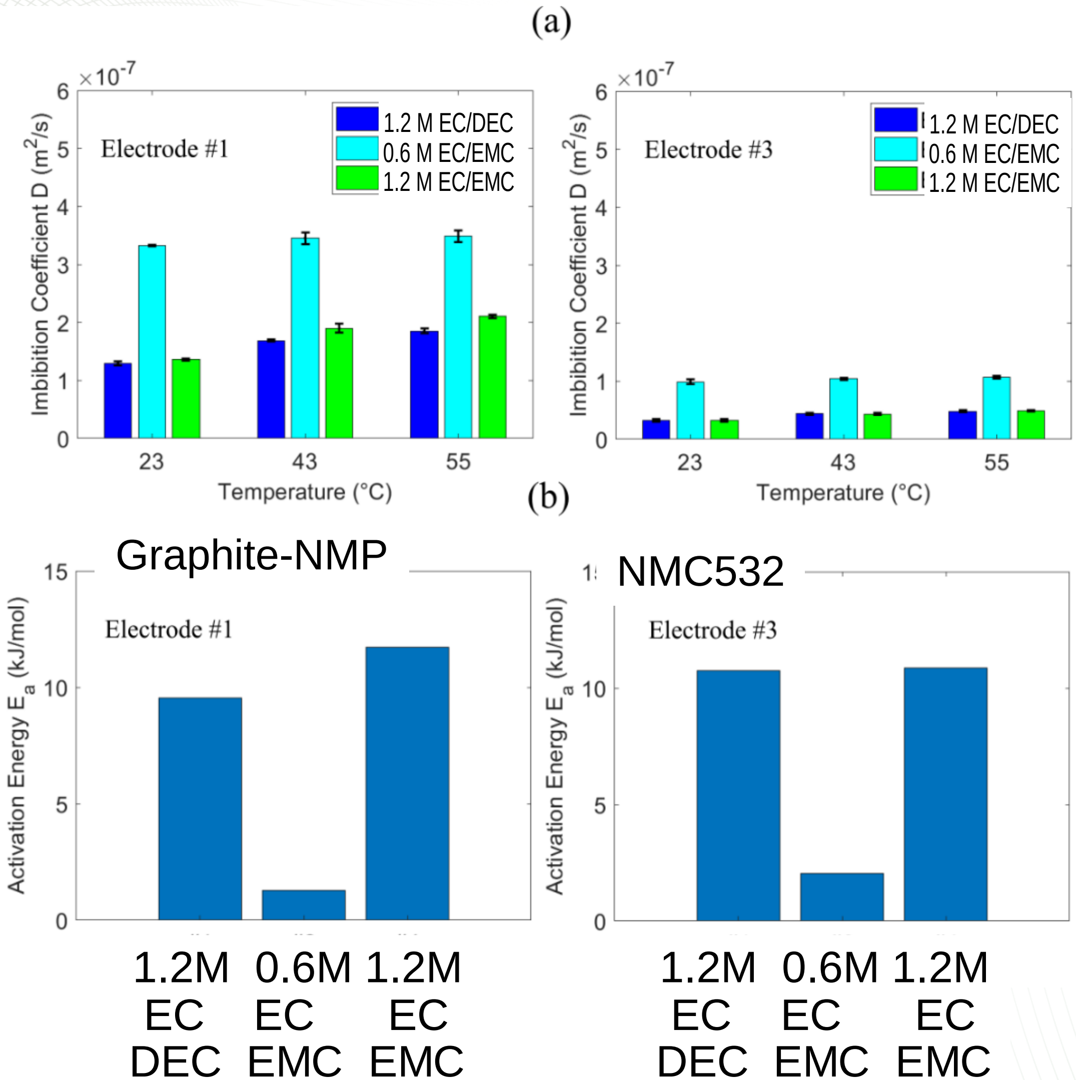
$$\text{Solid permeability coefficient (SPC)} = kB\cos\theta/(2\epsilon r_e)$$



- Electrolyte wetting was faster for NMP-processed electrodes than aqueous processed counterparts.
- Electrode wettability decreases with decreasing electrode porosity.
- Electrolyte imbibition is faster in graphite anode than NMC cathode.
- Electrolyte imbibition is faster with EC/EMC as solvent than EC/DEC.
- Increasing $LiPF_6$ content in electrolyte slows electrolyte imbibition due to increased viscosity.

Davoodabadi et al., Journal of Energy Storage 26 (2020) 101034

Technical Accomplishments—Characterizing the Activation Energy in Electrolyte Imbibition (FY20)



LiPF$_6$ in EC/EMC (3/7 wt) or EC/DEC (3:7 wt)

- Activation energy of electrolyte imbibition only depends on electrolyte composition and has no dependence on electrode properties.
- Activation energy is higher with increasing salt content indicating a more pronounced temperature dependence.

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Davoodabadi et al., Journal of Energy Storage 26 (2020) 101034

Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sandia National Laboratory, Idaho National Laboratory
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Active Material Suppliers: TODA America, Superior Graphite, Forge Nano
  - Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, Ashland, IMERYS
  - Equipment/Coating Suppliers: PPG Industries, Frontier Industrial Technology, B&W MEGTEC, DataPhysics
  - Universities: KIT, Binghamton University, University of Picardy Jules Verne
- Collaborative Activities
  - Characterization of surface energy and electrolyte wetting with Binghamton University (weekly)
  - Laser structuring of thick electrodes with KIT (monthly)
  - Synthesis of small NMC811 particles with Dr. Ozge Kahvecioglu Ferdun at ANL (BAT167)
  - Binder selection and optimization with Solvay, Ashland, and JSR (bi-annual)
  - Sharing of results with strategic battery manufacturers (Navitas Systems and XALT)
  - Electrolyte wetting study with University of Picardy Jules Verne (monthly)

Future Work

- Remainder of FY20
  - Continue fabricating structured Gen 3 thick NMC811 cathodes via aqueous processing; assemble 6-mAh/cm^2 pouch cells, obtain 500 0.33C/-0.33C cycles, and perform material and cell characterization such as EIS, XPS, etc.
  - Freeze cast 250-micron solid-state LLZO electrolyte (with 10-micron dense layer and 240-micron porous layer) and NMC 811 cathode (200 microns) with vertically aligned pore structures and successfully complete sublimation and infiltration steps.
- Into FY21
  - Freeze tape cast LIB Ni-rich NMC cathodes.
  - Optimize freeze tape casting conditions for low tortuosity electrode architecture.
  - Develop methods for densifying freeze-tape-cast electrodes.
  - Evaluate energy and power density of the electrodes.
  - Evaluate cathode and solid-state electrolyte interface.
- Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility; 3 total patents issued on aqueous processing methodologies.

Any proposed future work is subject to change based on funding levels.

Summary

- **Objective:** This project facilitates lowering the unit energy cost by **up to 17%** by addressing the expensive electrode coating and drying steps while simultaneously increasing electrode thickness.
- **Approach:** Develop green manufacturing with tailored electrode architectures to enable implementation of aqueous processed thick electrodes for high power performance.
  - Understand liquid-phase Li^+ mass-transport limitations in high energy electrodes.
  - Develop electrode formulation and processing to enable thick electrode manufacturing.
  - Develop tailored electrode architectures to overcome Li^+ mass-transport limitations.
  - Integrate aqueous processing with high-energy/high-voltage cathode materials.
  - Demonstrate and validate electrochemical performance in large format pouch cells.
  - Characterize surface energy of electrodes and evaluate electrolyte wetting in thick electrodes.
- **Technical:** Characterized compatibility of various cathode materials with aqueous processing; Fabricated thick, crack-free NMC811 cathodes (6-8 mAh/cm^2); demonstrated excellent rate performance and cyclability of aqueous processed NMC811 cathodes; improved rate performance of thick NMC811 cathode via 2-layer and laser structuring, respectively; fabricated crack-free NCA cathode via aqueous processing; correlated electrolyte imbibition and processing relationship.
- **Collaborators:** Extensive collaborations with national laboratories, universities, lithium-ion battery manufacturers, raw materials suppliers, and coating equipment manufacturers.
- **Commercialization:** 3 patents issued; high likelihood of technology transfer due to significant cost reduction benefits and equipment compatibility.

Selected Responses to Specific FY19 DOE AMR Reviewer Comments

- Reviewer 6 was curious with the binder binders used in aqueous processing, the pH of dispersion, rheological properties, stability of slurries and whether the cathode was surface coated.
  - **The binder was JSR TRD202A with CMC and PAA. The pH, rheological properties and stability of slurries have been reported previously and can be found in our previous AMR slides and publication.**
    - **Energy Storage Materials 24 (2020), 188-197**
    - **ACS Sustainable Chemistry & Engineering 8 (8) (2020), 3162**
  - **The cathode was uncoated and used as-received from Targray.**

- The reviewer 4 suggested that more optimization work should be performed including (1) water-to-solid mixture ratio; (2) ratio of the components in the solid mixture to active material to conductive carbon additive to binder; (3) size of the particles of the active material; (4) nature of the conductive carbon additive and the role of carbon surface functionalization; (5) time of mixing at various stages of the electrode fabrication, etc. The reviewer said that the performance of the aqueous-processed electrodes can be further improved by optimizing these and other electrode fabrication parameters. It is also important to note that these parameters need to be optimized for each electrode material individually. .
  - **Detailed optimization work was performed on $LiFePO_4$ in our previous work (2011-2014 VTO AMRs). We agree with the reviewer that the optimal processing conditions vary with different materials, and they need to be repeated. However, due to the limited resources and time, most efforts have been geared towards fabricating crack-free and thick aqueous processed NMC811 cathodes and demonstrating high energy and power density, which is a top priority of the project. We have planned to carry out the optimization work when time allows. In fact, some optimization work has been done as shown in slides 8-12.**

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Peter Faguy)

- ORNL Contributors:
  - David Wood
  - Claus Daniel
  - Zhijia Du
  - Ritu Sahore
  - Alexander Kukay
  - Blake Hawley
  - Kelsey Grady

Technical Collaborators:

- Ozge Kahvecioglu Ferdun
- Robert Wang
- Congrui Jin
- Alejandro Franco
- James Banas
- Gregg Lytle

Information Dissemination and Commercialization

- **7 Refereed Journal Papers and 1 issued patent**

1. W.B. Hawley, A. Parejiya, Y. Bai, H.M. Meyer, III, D.L. Wood, III, J. Li, "Lithium and transition metal dissolution due to aqueous processing in lithium-ion battery cathode active materials", *Journal of Power Sources*, Under Review, 2020.
2. D.L. Wood, III, M. Wood, J. Li, Z. Du, R.E. Ruther, K.A. Hays, C. Mao, and I. Belharouak, "Perspectives on the relationship between materials chemistry and roll-to-roll electrode manufacturing for high-energy lithium-ion batteries", *Energy Storage Materials*, Under Review, 2020.
3. J. Li, Y. Lu, T. Yang, D. Ge, D.L. Wood, III, Z. Li, "Water-based electrode manufacturing and direct recycling of lithium-ion batteries electrodes-a green and sustainable manufacturing system", *iScience*, *In Press*, 2020.
4. Y. Liu, X. Wang, J. Cai, X. Han, D. Geng, J. Li, and X. Meng, "Enhanced electrochemical performance of $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ cathode with atomic-scale tuned interface via atomic layer deposition of zirconium oxide", *Journal of Materials Science & Technology*, *In Press*, 2020.
5. R. Sahore, D.L. Wood, III, A.J. Kukay, K.M. Grady, J. Li, I. Belharouak, "Towards understanding of cracking during drying of thick aqueous-processed $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathodes", *ACS Sustainable Chemistry and Engineering*, **8** (2020) 3162-3169.
6. M. Wood, J. Li, R.E. Ruther, E. Self, H.M. Meyer, III, C. Daniel, I. Belharouak, D.L. Wood III, "Chemical stability and long-term cell performance of low-cobalt, Ni-rich layer oxide cathodes prepared by aqueous processing for high-energy lithium-ion batteries", *Energy Storage Materials*, **24** (2020) 188-197.
7. A. Davoodabadi, J. Li, H. Zhou, D.L. Wood, III, T.J. Singler, C. Jin, "Effect of calendering and temperature on electrolyte wetting in lithium-ion battery electrodes", *Journal of Energy Storage*, **26** (2019) 101034-101043.
8. Z. Du, J. Li, D.L. Wood, III, C. Daniel, Manufacturing of Thick Composite Electrode Using Solvent Mixtures, US Patent 10,601,027, Issued March 24, 2020.